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OFFICE OF NAVAL RESEARCH

Grant # N0001489J1848

R&T Code 413u002

Technical Report No. 9

A Comparison Study of Diamond
Films Grown on Tungsten Carbide Cobalt
Tool Inserts with CH₄ and CF₄ Gas Sources

by

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prepared for publication in the

Surface & Coatings Technology

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November 1992

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REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Nov. 1992	3. REPORT TYPE AND DATES COVERED Technical		
4. TITLE AND SUBTITLE A comparison study of diamond films grown on Tungsten carbide cobalt tool inserts with CH ₄ & CF ₄ gas sources		5. FUNDING NUMBERS G N0001489J1848 R&T code 413u002		
6. AUTHOR(S) K.J. Grannen, F. Xiong, R.P.H. Chang				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Science & Engr. Dept. Northwestern University 2225 Sheridan Road Evanston, IL 60208		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report # 9		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Chemistry Division Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>The results of a comparison study of continuous diamond coatings deposited on tungsten carbide-6% cobalt tool inserts using CF₄ and CH₄ gas sources are presented. The CH₄ grown diamond film utilizes a thin (1200 Å) amorphous silicon interlayer for adhesion while the CF₄ diamond film is deposited directly onto the tool insert. Diamond films produced with CF₄ gas have much higher growth rates and better adhesion than diamond films grown with CH₄ gas. The films are characterized by scanning and transmission electron microscopy, and Raman spectroscopy to determine film crystallinity and quality. Macroscopic indentation tests have been conducted to determine the adhesion of the films to the substrate, and an aluminum-17% Si alloy is machined with the diamond-coated tool inserts to determine their performance in a machining environment. A mechanism for the growth of diamond on tungsten carbide-cobalt using CF₄ gas is postulated.</p>				
14. SUBJECT TERMS Diamond films			15. NUMBER OF PAGES 32	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

A Comparison Study of Diamond Films Grown on Tungsten Carbide
Cobalt Tool Inserts with CH₄ and CF₄ Gas Sources

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ABSTRACT

The results of a comparison study of continuous diamond coatings deposited on tungsten carbide-6% cobalt tool inserts using CF₄ and CH₄ gas sources are presented. The CH₄ grown diamond film utilizes a thin (1200 Å) amorphous silicon interlayer for adhesion while the CF₄ diamond film is deposited directly onto the tool insert. Diamond films produced with CF₄ gas have much higher growth rates and better adhesion than diamond films grown with CH₄ gas. The films are characterized by scanning and transmission electron microscopy, and Raman spectroscopy to determine film crystallinity and quality. Macroscopic indentation tests have been conducted to determine the adhesion of the films to the substrate, and an aluminum-17% Si alloy is machined with the diamond-coated tool inserts to determine their performance in a machining environment. A mechanism for the growth of diamond on tungsten carbide-cobalt using CF₄ gas is postulated.

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I. INTRODUCTION

The unparalleled physical properties of diamond have driven researchers to synthesize diamond crystals and thin films. Recently and more specifically, the chemical vapor deposition (CVD) method, in forms such as microwave plasma CVD¹, RF plasma CVD², hot filament CVD³, electron assisted CVD⁴, laser assisted CVD⁵, DC plasma CVD⁶, and plasma jet CVD⁷, has received intensive investigation due to the possibility of the direct deposition of diamond films on a variety of substrates. Research and development interests are found in the electronics, aerospace, cutting tool, and related industries. For the cutting tool industry, the high hardness and thermal conductivity of diamond as well as the possibility of coating a variety of cutting tool shapes, a notable deficiency in polycrystalline diamond (PCD) technology, make CVD diamond an attractive alternative. Materials likely to be machined include Al-Si alloys, composites, ceramics, and various wood-based products. In fact interest in diamonds is escalating rapidly, and the average market for abrasive diamond, not to mention diamond's electronic or tribological markets, is expected to be \$200 million by 1995⁸. While the forecasts look promising, many issues and problems remain to be solved.

In this paper, we present our research results on the CVD of diamond on tungsten carbide - cobalt (WC-Co). One of the most serious problems to be solved concerns the poor adhesion of the diamond film to the WC-Co substrate. Recent work on diamond

coating of cemented carbides has focused on two main issues: 1) Removal of near-surface cobalt by chemical⁹ or plasma¹⁰ etching to allow diamond deposition to proceed and 2) improvement of the coating substrate adhesion by various means. Adhesion strength improvement is accomplished by diamond seeding¹¹⁻¹² and pre-decarburization of the WC.¹³ These methods serve to increase the nucleation density thereby improving the bond between the substrate and the coating. Soderberg et.al.¹⁴ have concluded three reasons account for the poor adhesion: void formation during growth, non-diamond material formation at the interface, and high residual compressive stresses in the deposited film. The ability to improve the interface adhesion depends upon the type of interface found and/or needed. Chalker et.al.¹⁵ depict three main types of interfacial zones occurring between a coating and a substrate. The first results from pseudo-diffusion brought about by monolayer by monolayer deposition. Secondly, an interlayer is used to promote bond formation between the two regions, and finally, a rough interface causes mechanical keying and locking between the coating and the substrate. In this research, a comparison study of the improvement of the interface adhesion of unseeded diamond coating on WC-Co has been undertaken by using an a-Si interlayer for CH₄ growth and chemical pre-treatment for CF₄ growth.

II. EXPERIMENTAL

Diamond growth in this experiment utilized a microwave plasma enhanced CVD setup described previously.¹⁶ No independent substrate heating was used; the plasma itself heated the substrate to the growth temperature of approximately 900° C. No substrate pre-treatment with diamond powder was used in any of the experimental samples. The typical diamond growth conditions are listed in Table I.

To determine what effect the etchants have on subsequent diamond growth, the tool inserts (Ingersoll Cutting Tools grade 110) of WC-Co (6% Co) have been treated either by cobalt etching, ($\text{FeCl}_3\text{:H}_2\text{O}$ 1:33 by weight) tungsten carbide etching, ($\text{K}_3\text{Fe(CN)}_6\text{:NaOH:H}_2\text{O}$ 1:1:10 by weight) or both cobalt and tungsten carbide etching. Subsequent diamond growth proceeded for 1/2 hour with 3% CF_4 or 1/2% CH_4 . For continuous diamond coatings, tool inserts were initially prepared in two groups. One group received a surface roughening treatment while the other group acquired an amorphous silicon interlayer on the tool insert surface. The roughening treatment consisted of sequentially etching the tungsten carbide and the cobalt. An amorphous silicon interlayer (approx. 1200 Å thick) was deposited by RF decomposition of a 2% silane balance hydrogen gas mixture.

The analysis of diamond coatings was conducted by a variety of techniques. Auger electron spectroscopy (AES) determined the surface elements present during the various steps in the etching

of the tool inserts and growth of the diamond on the tool inserts. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to visually observe the nucleation density, the grain size and structure of the diamond . The purity/crystallinity of the films was determined by Raman spectroscopy with the 488 nm Ar⁺ line.

To evaluate the macroscopic adhesion of the films to the substrate, indentation tests were conducted with loads ranging from 15 kg to 60 kg in 15 kg increments utilizing a "N" Brale indenter and associated hardness tester similar to tests performed by Jindal et.al.¹⁷. For each indentation, crack lengths were measured at 45° intervals around the indentation; the eight values were averaged to yield an average crack length value for that indentation. Seven to nine indentations were made for each data point. Finally, a real cutting test was conducted on 390 aluminum, an alloy containing 17% Si, to evaluate the coatings in a real machining environment. The machining conditions are listed in Table II. After the cutting tests, the wear lands, wear land lengths, and wear depths were measured with an optical microscope and profilometer respectively. Using these measurements, the volume wear rate of the tool insert during the cutting test is determined by plotting the wear volume versus the cutting time.

III. RESULTS

1. Diamond Nucleation and Growth

Fig. 1 details the nucleation densities for the various combinations of etchants and source gases without diamond pre-seeding. In the first case, the cobalt has been etched away and diamond nucleated using 3% CF_4 (Fig. 1a) and 1/2% CH_4 (Fig. 1b). It is found that the diamonds in Fig. 1a are much denser and larger with a wide variety of crystal sizes evident when compared to Fig. 1b. One may argue that six times more carbon in the CF_4 than the CH_4 case may have enhanced nucleation of the larger and denser crystals; however, an identical test conducted with 3% CH_4 yielded no diamond crystals but a continuous layer of soot on the surface. Apparently different nucleation and growth mechanisms are at work for the two gas sources.

In the second case, the WC crystals of the tool inserts were preferentially etched. This etching produces a wide variety and quantity of sharp edges, steps, and crevices, all ideal places for diamond nucleation. Compared to the previous case, the nucleation density is reduced on both samples. The 1/2% CH_4 sample (Fig. 1d) exhibits practically no diamond crystals while the CF_4 sample (Fig. 1c) has some diamond crystals. This indicates that a different mechanism is taking place to allow nucleation to occur in the presence of surface cobalt.

Using the two etchants concurrently to remove the cobalt and roughen the tungsten carbide results in typical nucleation densities shown in Figs. 1e and 1f. The CF_4 growth sample (Fig.

1e) contains a dense pattern of very small crystals, much smaller than either of the other CF_4 grown samples. This high nucleation density implies, in the long run, a better film-substrate adhesion due to the increased contact area between the film and the substrate as well as fewer voids as the crystals grow to form a continuous film. Nucleation to this degree without a pre-treatment indicates that some substrate-plasma interaction is occurring that aids in the diamond nucleation. Relatively few crystals are seen in the sample grown with 1/2% CH_4 (Fig. 1f).

This is not surprising because of the lack of a diamond powder pre-treatment as a conventional diamond growth pre-treatment. On a longer time scale, diamond coatings on tool inserts etched as in Fig. 1e and 1f have very different appearances. A continuous film 3-4 μm thick is deposited after two hours with CF_4 while 8 hours of growth with CH_4 yields a discontinuous film with a large graphitic component.

Fig. (2) gives the Auger spectra of an etched tool insert and an etched tool insert exposed to a 3% CF_4 diamond growth plasma for 5 minutes. Upon etching the tungsten carbide and cobalt, a variety of elemental species is found. The resultant Auger spectrum is shown in Fig. 2a. Peaks identified include tungsten at 169 and 179 eV with chlorine at 181 eV, overlapping the 179 eV tungsten peak. Other peaks of interest include the carbon fine structure at 252, 260, and 271 eV showing the carbidic nature of the sample, nitrogen at 379 eV, and oxygen at 468, 483, and 503 eV. Metallic species, other than tungsten,

present on the surface are iron at 598, 651, 703, and 716 eV, and cobalt at 775 eV. All of these new elements, except for oxygen, are residues from the etching process. The oxygen peak is due to both etching and environmental adsorption. The etching process yields adherent residue films (i.e. films not easily removed from the substrate by methanol or acetone rinsing.) The cobalt is bound with the chlorine to form cobalt chloride, while the tungsten most likely forms tungsten oxides, with tungsten pentoxide (W_2O_5) being stable to around 800° C.

A tool insert with a WC and Co etch followed by an exposure to a diamond growth plasma for 5 minutes has a typical Auger spectrum shown in Fig. 2b. This spectrum exhibits tungsten, carbon, and oxygen peaks all at the characteristic energy values found in Fig. 2a while the cobalt, iron, chloride, and nitrogen peaks associated with the chemical etching have disappeared. The highly reactive hydrogen atoms in the plasma readily remove the surface and near-surface layer of contaminants paving the way for commencement of diamond growth.

Having some idea how etching affects the surface of the tool inserts, continuous films were grown and characterized for crystallinity and purity. The results of the TEM analysis conducted on films grown with CH_4 and CF_4 are found in Fig. 3. This figure contains plan-view, bright-field TEM micrographs and corresponding electron diffraction patterns for diamond grown with CH_4 (Fig. 3a) and CF_4 (Fig. 3b). Large, well-faceted crystals ($> 1\mu m$) are found when growing with a CH_4 precursor.

The selected area electron diffraction pattern gives a polycrystalline pattern with diffraction rings from the diamond (111), (220), and (311) planes (1st, 3rd, and 4th rings from the center) and from the graphite (1012) plane (2nd ring) indicating that a significant amount of graphite exists in this film. Smaller crystals are seen in the CF_4 grown diamond in Fig. 3b. This is consistent with the results shown in Fig. 1e. The electron diffraction pattern in Fig. 3b shows only the well-defined rings of spots indicative of polycrystalline diamond; no graphite ring is found. The explanation for the absence of the graphite ring when growing with CF_4 could be due to a more efficient etching of the graphite when growing with CF_4 or a different growth process. The discussion section details these possibilities.

2. Growth of Continuous Diamond Coatings

Due to the slow growth of diamond on WC-Co when using CH_4 , an interlayer of a-Si was deposited to aid in diamond nucleation. The thought is to use the a-Si to create a thin layer of silicon carbide and then have the diamond grow on top of the silicon carbide. A continuous film is grown over the entire substrate. Using CF_4 on an a-Si interlayer results in destruction of the interlayer because CF_4 plasmas etch silicon quite readily. As a result, diamond growth with CH_4 source gas on a substrate with an interlayer, is compared to diamond growth with CF_4 source gas on a chemically etched substrate. In the

remainder of the paper, the reference to CH_4 refers to diamond growth on an a-Si interlayer deposited on WC-Co while CF_4 refers to diamond growth on a chemically etched WC-Co substrate.

The crystallinity of the films determined by Raman spectroscopy is shown in Fig. 4a for the CH_4 grown diamond and Fig. 4b for the CF_4 grown diamond. For the CH_4 sample, the characteristic diamond peak at 1332 cm^{-1} is present but it is very broad and weak in intensity. The FWHM value of the peak is 19 cm^{-1} indicating deviations from a perfect crystal lattice. This broadening can be attributed to defects in the diamond crystals brought about during the growth process.¹⁸⁻¹⁹ This small peak also indicates the difficulty in nucleating and growing diamond on an unseeded substrate. It is not surprising that a large graphite peak is found centered around 1580 cm^{-1} , which dovetails with the electron diffraction pattern shown previously.

For the CF_4 grown samples, the Raman spectra (Fig. 4b) is somewhat different. The characteristic diamond peak at 1332 cm^{-1} is much stronger in intensity and more narrow (FWHM = 8 cm^{-1}) when compared to the CH_4 diamond. Some graphitic components are also detected as seen by the small, broad "hump" centered around 1580 cm^{-1} , but the quantity of graphite is small when the intensities of the graphite and diamond peaks and the scattering coefficients of graphite and diamond (50:1) are taken into consideration.

Shown in Fig. 4 are two SEM micrographs examination of

the deposited coatings which reveal a different crystal morphology for the two samples (a: CH_4 b: CF_4). Both were grown at the same measured substrate temperature (900 C), but for different times as listed in Table I. The (111) facets are found for the CH_4 case and (100) facets for the CF_4 case. The preponderance of (100) facets on the CF_4 sample is rather surprising at this carbon concentration. An investigation of the growth of diamond on silicon using CH_4 source gas indicates that the (100) morphology terminates around a concentration of 1.2% CH_4 ²⁰. In the CF_4 diamond case, (100) facets are still found at a carbon concentration 2.5 times higher. Even higher concentrations of CF_4 (6%-9%) produce a microcrystalline morphology. Reasons for this occurrence are not entirely clear at this time.

3. Adhesion and Machining Performance of the Diamond Coatings

The micrograph inset into figure 5 is a low magnification view of an indentation. The circular area in the center of the film is the point of contact between the indenter and the film. Around this contact zone is the portion of the film that has delaminated due to the applied load. The scale of the figure gives an indication of the macroscopic nature of this indentation test.

Figure 5 is a plot of the crack lengths of indentations vs. the load depicting the wide adhesion disparity between the CH_4

and CF_4 grown diamond. The test results from diamond grown on a-Si deposited on the tool insert (curve a) and literature values of diamond grown with pre-seeding¹¹⁻¹² (curve b) exhibit rather large crack lengths. The crack length in the CF_4 grown diamond coating (curve c) monotonically increases with the load approaching 150 microns at 60 kg of load compared to 400 microns at 45 kg of load in the CH_4 case. Throughout this test the adhesion of the CF_4 films is found to be a factor of two or more better than for the CH_4 films.

Fig. 6 shows optical micrographs of tool insert wear of a virgin tool insert (a), an uncoated insert machined for 8 minutes (b), and a diamond coated insert machined for 8 minutes (c). A long, narrow wear land appears on the uncoated sample (Fig. 6b) while a shorter but somewhat wider wear pattern is found on the diamond coated insert (Fig. 6c). Initially the diamond coating along the cutting edge provides protection and shifts the wear pattern back along the top face of the tool insert. With no diamond coating, wear can proceed quite easily in the vertical direction as well as back down along the cutting tool.

The volume of tool insert abraded away by the material being cut is plotted versus the cutting time, shown in Fig. 7. Each data point is the result from one tool insert machined for a specified length of time. Four tool inserts of the same type were used for each curve resulting in some spread of the experimental data. A least square fit was performed to find the trend of the data. All three curves start in the same general

vicinity. After one minute, very little difference is seen in the abraded wear volume. After a longer cutting time, differences begin to appear. The volume wear rates (slope of each curve) are as follows: $.31 \mu\text{m}^3/\text{min}$ for the uncoated sample (a), $.24 \mu\text{m}^3/\text{min}$ for the CH_4 diamond coated sample (b), and $.20 \mu\text{m}^3/\text{min}$ for the CF_4 diamond coated sample (c). A 50% improvement in the volume wear rate is seen between an uncoated and a CF_4 diamond coated tool insert. Correlating the wear rate to the indentation results, one realizes that a better indentation adhesion value corresponds to a better wear volume. Further improvements in cutting performance may be possible by thoroughly understanding how CF_4 nucleates and grows diamond on WC-Co without a diamond powder pre-treatment.

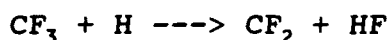
Comparison with other researcher's experimental data is difficult due to the variability in cutting materials and conditions. For example, in other papers cutting depths and speeds range from 0.5 mm and 450 m/min on an Al-11.7% Si rod¹⁰ to 0.1 mm and 250 -350 m/min on an Al-11% Si rod¹². Still others used 0.5 mm and 200 m/min on an Al-20% Si alloy²¹ and 1.5 mm, 300 m/min on an Al-18% Si alloy¹⁴. Comparison with other types of materials is clearly inappropriate (i.e. Al-11% Si), but similar materials (i.e. Al-18% Si & Al-20% Si) have higher cutting speeds (33-100% higher) and a lower depth of cut in one case and slightly higher in another. To allow for comparison among researchers, it seems to be necessary to standardize some type of testing procedure for machining diamond coated tool inserts.

IV. DISCUSSION

Our experiments have shown that high quality diamond coatings can be grown with 3% CF_4 compared to diamond grown with 1/2% CH_4 on an a-Si interlayer. Knowing some facts about the film composition, structure, and morphology as well as previous work different growth mechanisms can be postulated for CH_4 nucleation on a-Si and CF_4 diamond nucleation directly on the WC. The probable growth mechanism when using CH_4 gas involves conversion of portions of the a-Si to form silicon carbide and tungsten silicide. The WSi_2 forms at the interface between the a-Si and the WC serving as an adhesive layer while the silicon carbide forms from a reaction of the gaseous carbon species and the a-Si. This nascent SiC then serves as a nucleation site for the diamond growth in much the same way as diamond nucleation on single crystal silicon where a thin silicon carbide layer is formed before diamond nucleation and growth begins²²⁻²³. The large size of the crystals, as indicated by TEM micrographs, implies a low initial nucleation density. The low nucleation density also means a long growth period will be needed to allow the crystals to coalesce into a continuous film. While the crystals are growing to form a continuous film, the gaps between the crystals are still subjected to a carbon flux. Unable to attach to a diamond nuclei, the incoming carbon is deposited as graphite and amorphous carbon. As a result, a two phase region is initially

formed in the film. The amount of oxygen used is obviously unable to remove all of the graphite co-depositing on the continuous diamond film. The end result is a diamond film containing diamond crystals as the majority constituent, but also some graphite and amorphous carbon components.

Little work has been done regarding the mechanism for the growth of diamond with CF_4 source gas²⁴⁻²⁵, and certainly no work has been done regarding CF_4 growth of diamond on WC-Co tool inserts. Based on our experimental results the mechanism of growth is postulated. Plumb and Ryan²⁶⁻²⁷ have conducted several experiments to determine the species present in a $\text{CF}_4\text{-H}_2$ and $\text{CF}_4\text{-O}_2$ discharge. For the $\text{CF}_4\text{-H}_2$ experiment the dominant reaction was as follows:



The CF_3 came from the dissociation of CF_4 either from electron impact or from the reaction with atomic hydrogen in the plasma. In the $\text{CF}_4\text{-O}_2$ discharge, the CF_4 is dissociated into CF_3 and CF_2 . Through a complex reaction sequence, the CF_3 and CF_2 react with oxygen in the discharge and form the following stable carbon-containing species: COF_2 , CO_2 , and CO . The concentration of these stable species varies according to the ratio of CF_4 and O_2 in the discharge. Growing diamond on WC-Co with a combination of H_2 , O_2 , and CF_4 results in a variety of plasma species, and these species may be a combination of the species found separately in

the $\text{CF}_4\text{-H}_2$, and $\text{CF}_4\text{-O}_2$ plasmas described above. Work is in progress to identify the species present in the plasma, their concentrations as well as the role of the carbon containing species in the nucleation and growth of diamond films.

Several reasons may explain the better adhesion strength. Smaller crystal sizes for the CF_4 grown diamond means fewer voids and more film-substrate interface area implying better film-substrate adhesion. Less non-diamond component for the CF_4 grown diamond may also result in improved adhesion strength. Should the proposed growth mechanism detailed in the above be proven correct, CF_4 grown diamond results in a strong bond between the WC substrate and the diamond film itself.

V. CONCLUSION

Interlayers of a-Si for CH_4 diamond growth and surface chemical pre-treatment for CF_4 diamond growth have been used to improve the adhesion between the diamond film and the WC-Co tool insert. In both cases, no pre-seeding with diamond powder is required. Analytical characterization of the films shows the CF_4 film to contain small crystals and less graphite when compared to the CH_4 grown film. Diamond films grown on WC-Co with CF_4 also have a growth rate approximately four times faster than diamond films grown on WC-Co with CH_4 . Indentation testing shows an increased adhesion strength by a factor of two or more for the CF_4 grown film. Machining tests on 390 aluminum depicts the increased durability of the CF_4 grown films when compared to the

CH₄ grown films and plain, uncoated inserts. Further understanding of the CF₄ growth mechanism may result in additional adhesion improvements.

ACKNOWLEDGEMENT

The authors would like to thank Dean Edwards and his staff at Ingersoll Cutting Tools for providing and machining the tool insert samples. This work is supported by the Department of Energy under contract number DE-FG02-87ER45314 and the Office of Naval Research.

TABLE I. EXPERIMENTAL DIAMOND GROWTH CONDITIONS

Substrate:		WC/ 6% Co
Surface Modification:		Chemical etching with $K_3Fe(CN)_6:NaOH:H_2O$ 1:1:10 or an a-Si interlayer
Feed Gases:	(1.)	1/2% CH_4 , 1% O_2 , balance H_2
	(2.)	3% CF_4 , 1% O_2 , balance H_2
Total Flow Rate:		200 sccm
Pressure:		40 mBar
Microwave Power:		350 - 400 W
Substrate Temperature:		900 C
Growth Time:		8 hrs. for 1/2% CH_4 2 hrs. for 3% CF_4

TABLE II. CUTTING TEST PARAMETERS

Machine Parameters:

Speed: 152 m/min
 Feed: 0.254 mm/revolution
 Depth of cut: 1.27 mm
 Cutting Time: 1, 2, 4, and 8 minutes
 Coolant: None

Workpiece:

Material: 390 Aluminum
 Hardness: < 20 HrC (as cast)
 Actual Material Composition: Shown in table below (%)

Si	Fe	Cu	Mn	Cr	Ni	Zn	Ti
16.9	0.29	4.9	<.01	<.01	<.01	<.01	.13

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FIGURE CAPTIONS

Figure 1. SEM micrographs showing diamond nucleation densities after various chemical etching and growth procedures. (a) and (b) are etched for 4 hrs in FeCl_3 , (c) and (d) for 2 min. in Murakami's etchant, and (e) and (f) are etched with both. In terms of growth, (a), (c), and (e) are grown with 3% CF_4 for 1/2 hr, and (b), (d), and (f) with 1/2% CH_4 for 1/2 hour.

Figure 2. Auger spectra of (a) WC-Co etched with Murakami's etchant for 2 min. and FeCl_3 for 4 hrs., and (b) a WC-Co sample with the same etching treatment as (a) but exposed to a 3% CF_4 diamond growth plasma for 5 min.

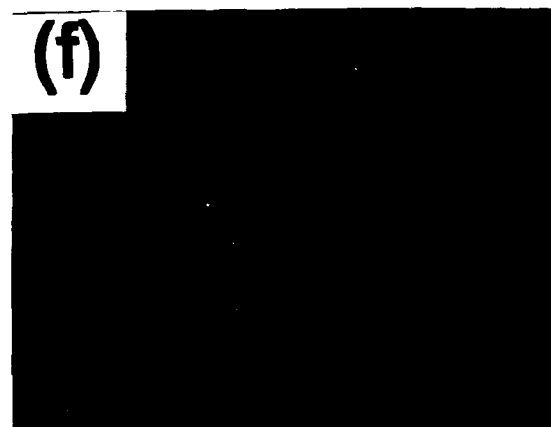
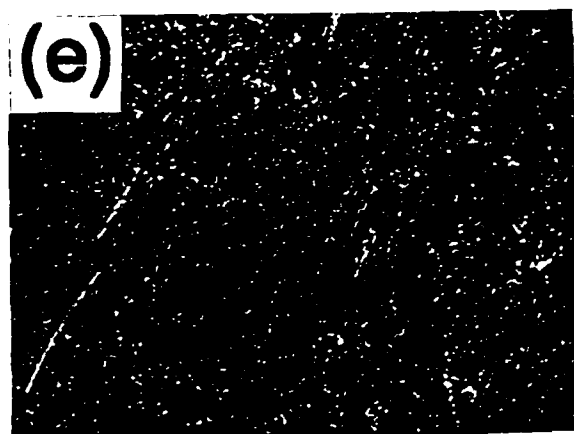
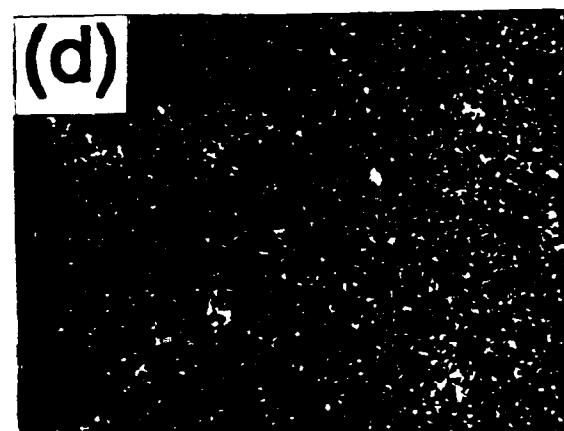
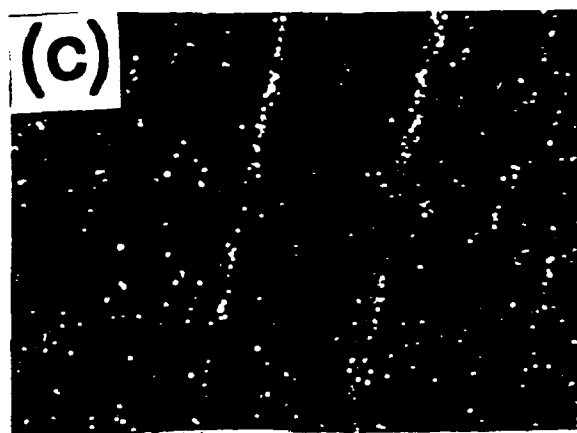
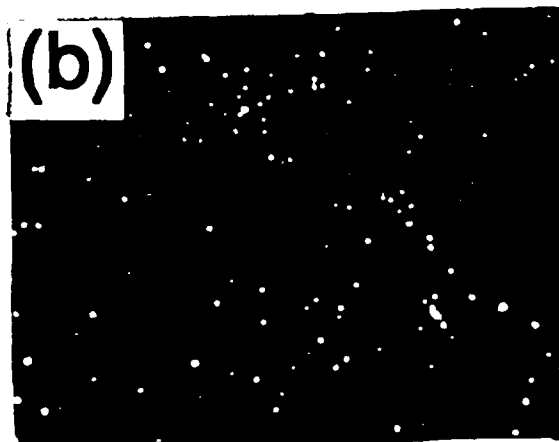
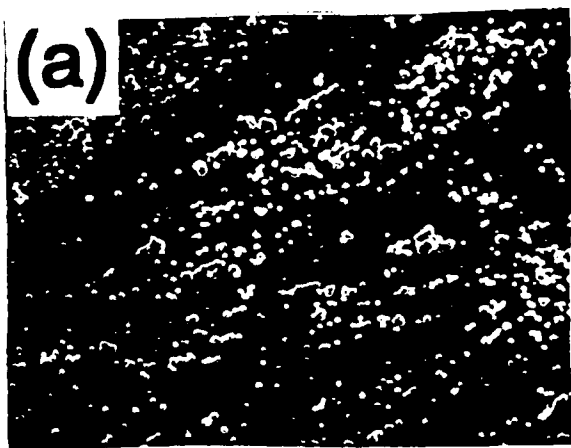
Figure 3. Plan-view bright-field TEM micrographs and corresponding electron diffraction patterns for diamond film grown with CH_4 precursor (a), and CF_4 precursor (b).

Figure 4. Raman spectra and SEM micrographs of diamond films grown with (a) 1/2% CH_4 and (b) 3% CF_4 .

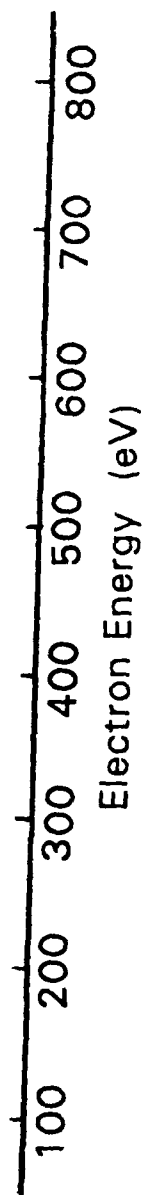
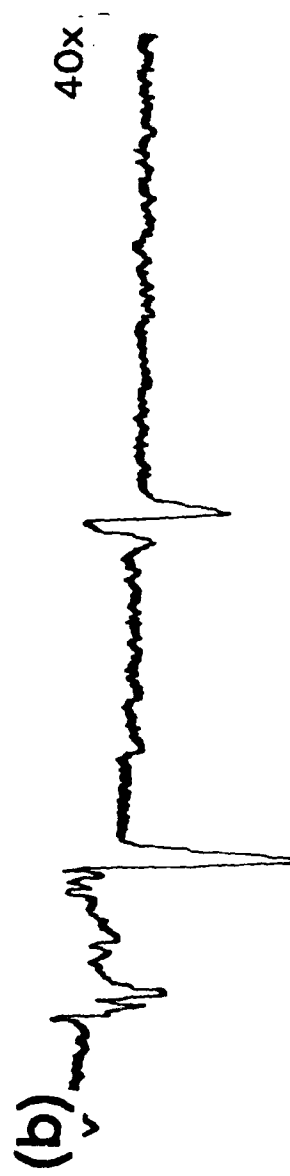
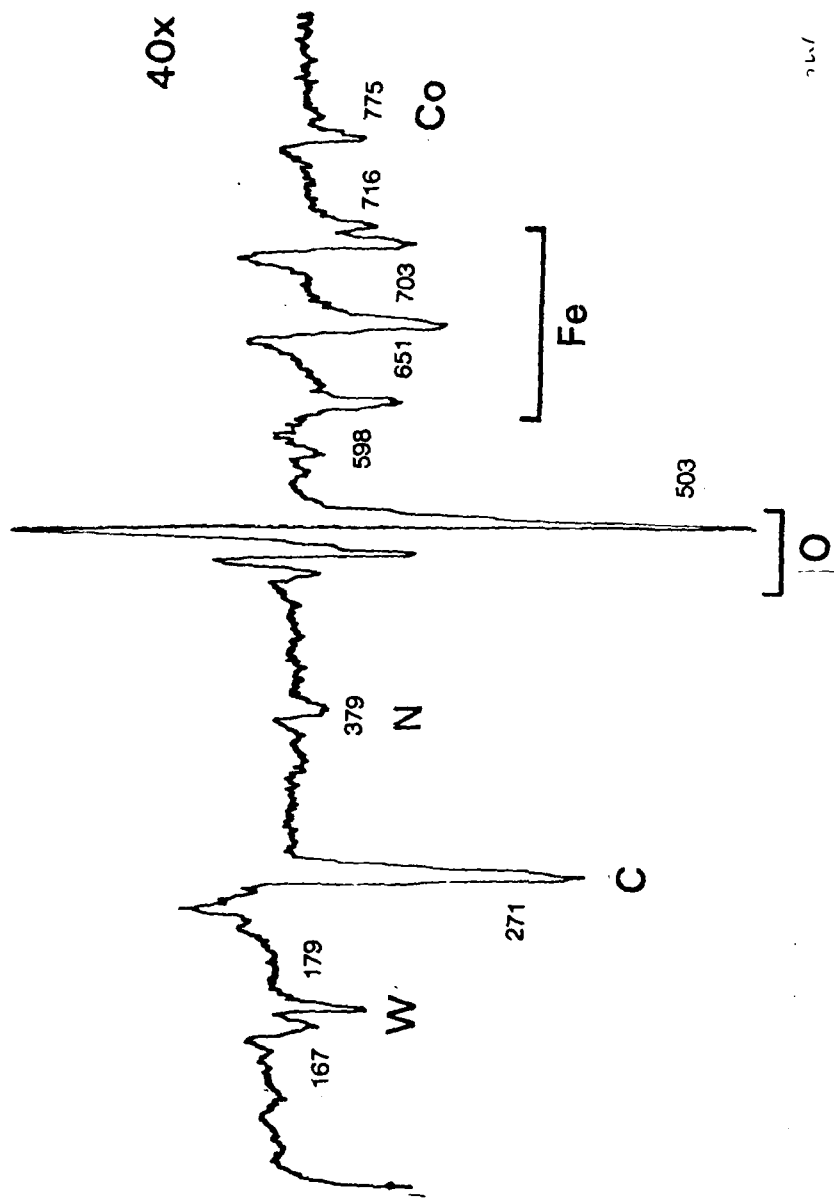
Figure 5. Indentation adhesion test results for various diamond films grown on WC-Co tool inserts. (a) 1/2% CH_4 , (b) experimental data from Ref. 12, and (c) 3% CF_4 .

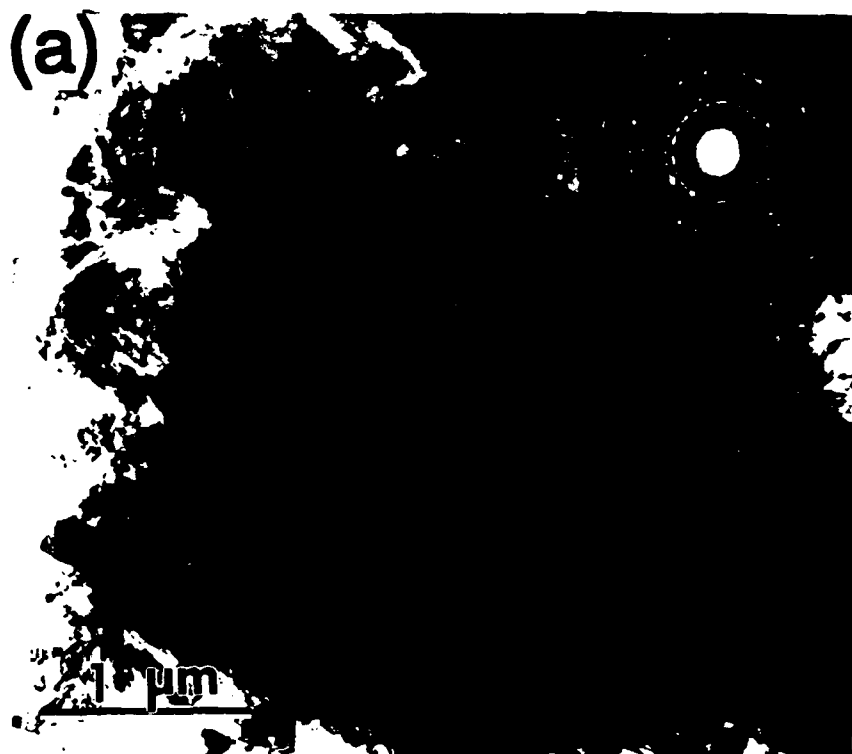
Figure 6. Optical micrographs of tool inserts after machining Al-17% Si for various times. (a) uncoated, unmachined, (b) uncoated, machined for 8 minutes, (c) diamond coated, machined for 8 minutes.

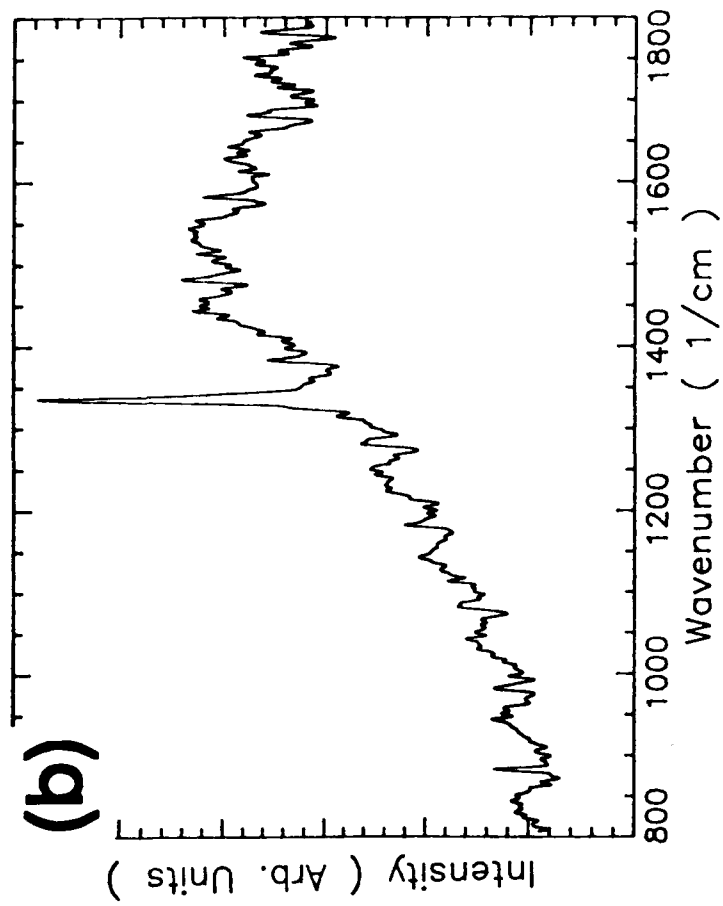
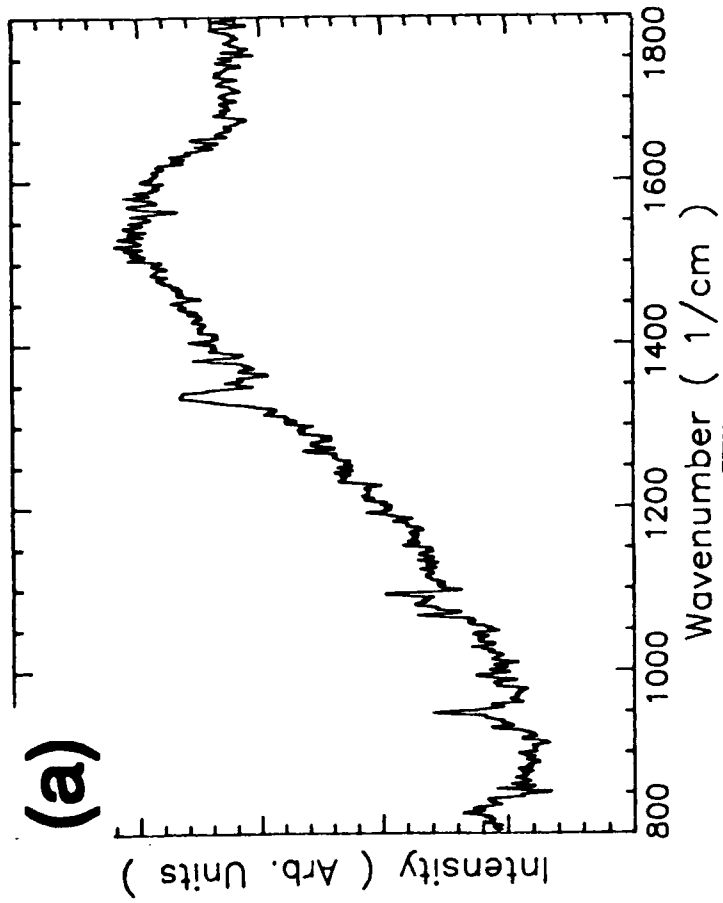
Figure 7. Amount of tool insert volume worn away with respect to cutting time for various coated and uncoated tool inserts. The curves are (a) uncoated insert (+), (b) 1/2% CH_4 diamond coating (○), (c) 3% CF_4 diamond coating ().

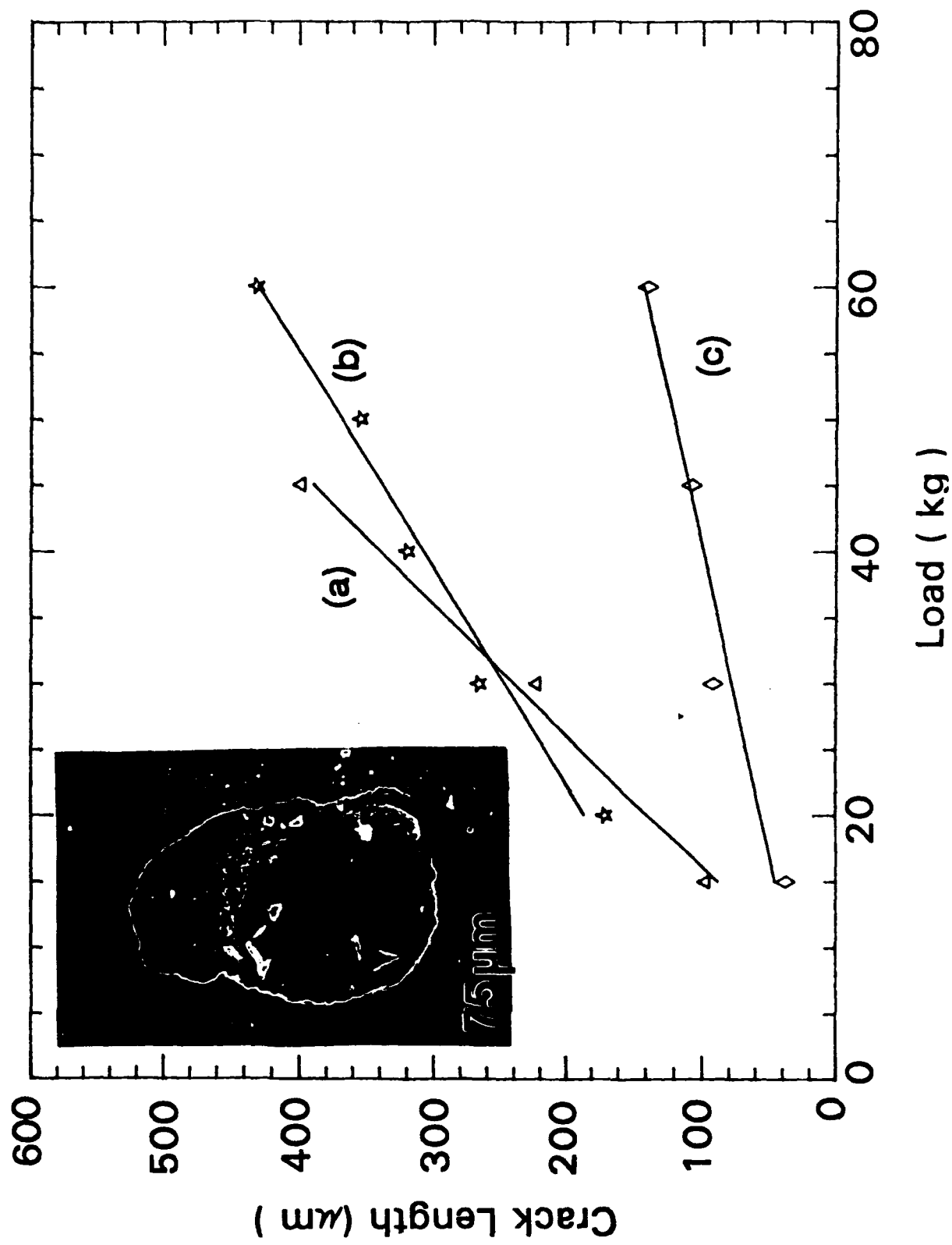


50 μm

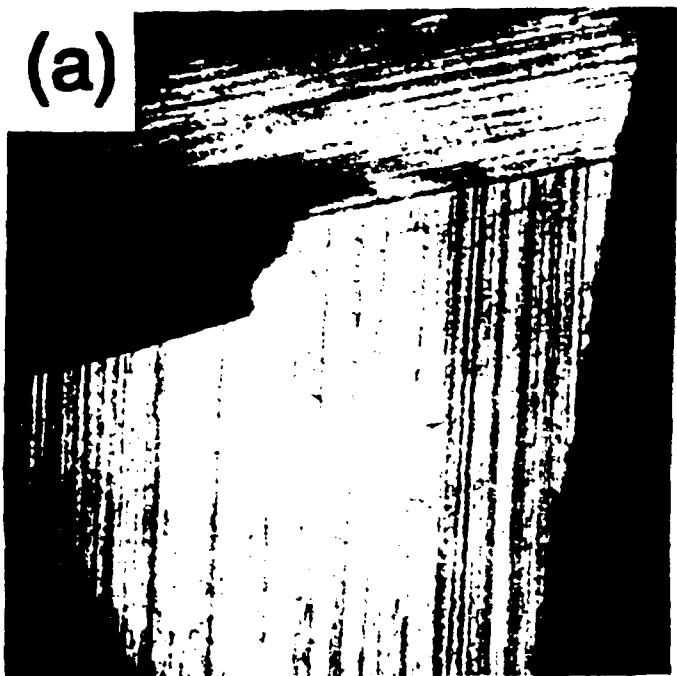




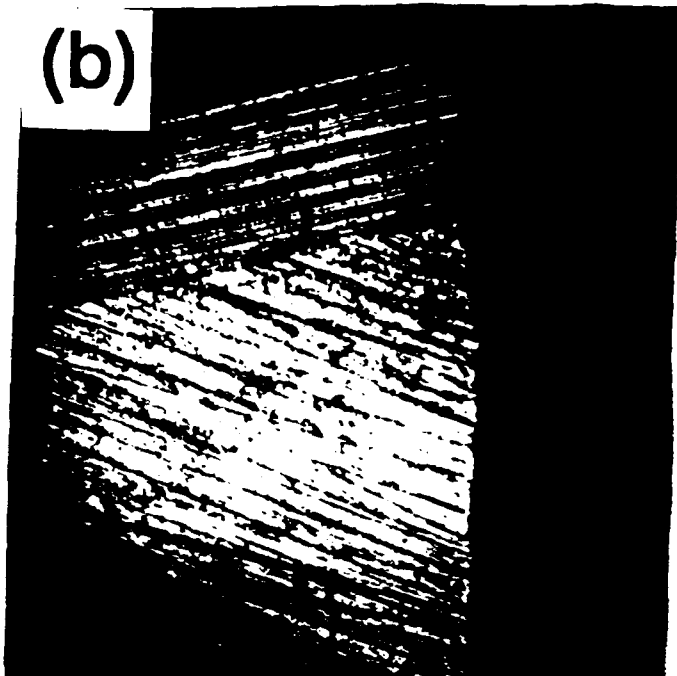




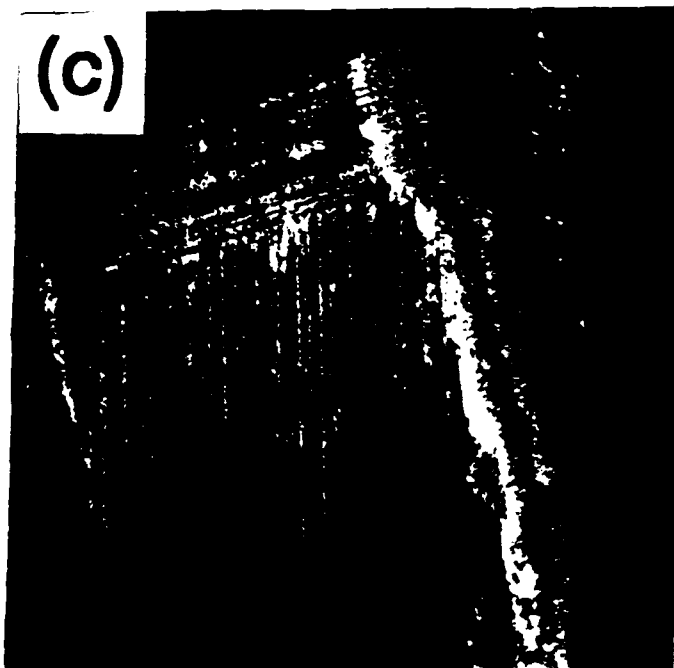
(a)

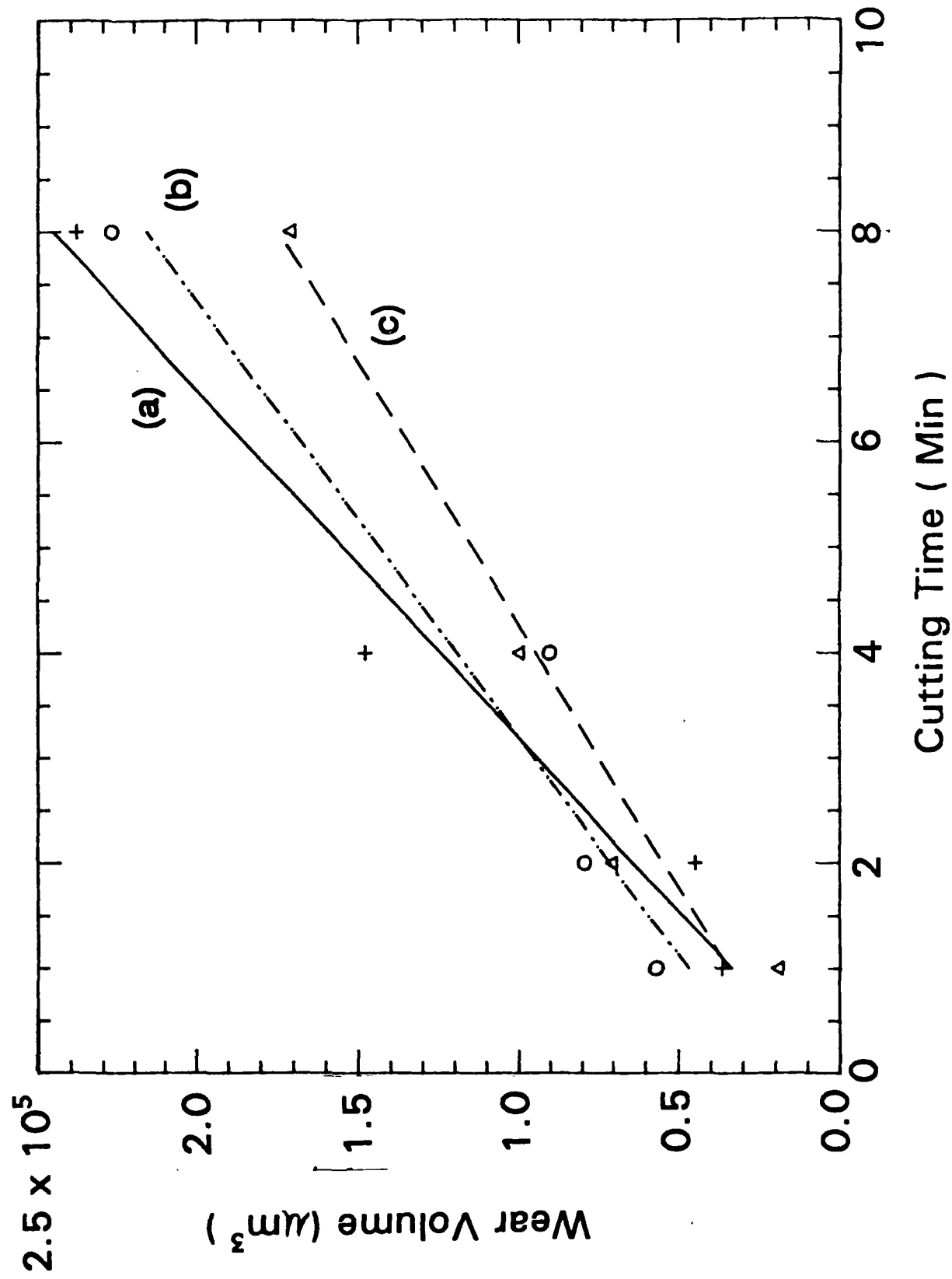


(b)



(c)





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